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# Crystal structure and magnetic properties of the compound MnN

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## Abstract

The compound MnN was prepared as a single phase by DC reactive sputtering. Its crystal structure is determined to be face-centered tetragonal one with the NaCl type by X-ray diffraction measurements. The compound MnN is stable up to 753 K and decomposes to tetragonal  $Mn_3N_2$  at 758 K. This compound exhibits a antiferromagnetism. © 2000 Published by Elsevier Science S.A. All rights reserved.

Keywords: MnN; Crystal structure; Magnetic properties

#### 1. Introduction

It is known that there are four stable intermediate phases ( $\varepsilon$ ,  $\zeta$ ,  $\eta$ ,  $\theta$ ) in the Mn–N system. The  $\varepsilon$  phase has a face-centered cubic structure (f.c.c.), the  $\zeta$  phase a hexagonal closed packed one (h.c.p.). The  $\eta$  and  $\theta$  phases have face-centered tetragonal structures (f.c.t.). Mn<sub>4</sub>N [1–3] belongs to the  $\varepsilon$  phase. Mn<sub>5</sub>N<sub>2</sub> [1,4], Mn<sub>2</sub>N [2,5] and Mn<sub>2</sub>N<sub>0.86</sub> [6] belong to the  $\zeta$  phase.

 $Mn_3N_2$  [1,4,7] belongs to the  $\eta$  phase. It is considered that MnN belongs to the  $\theta$  phase [1]. These compounds are prepared by reacting  $N_2$  or  $NH_3$  with Mn powder at high temperatures in most cases.

Nishiyama et al. prepared Mn nitrides by nitriding Mn powder with ammonium [8]. Among the prepared samples, they found the MnN compound which has f.c.c. structure with lattice constant a=4.435 Å (=51 at.%N).

Lihl et al. prepared a series of Mn–N compounds with 20.9–47.9 at.% N by reacting N<sub>2</sub> or NH<sub>3</sub> with Mn amalgams [1]. The most N-rich phase (with 45.7–47.9 at.% N) has a f.c.t. crystal structure with the lattice constants a=4.221 Å, c=4.113 or 4.115 Å (45.8 at.% N) and a=4.214 Å, c=4.148 Å (47.9 at.%N).

Otsuka et al. prepared polycrystalline Mn-N films with a

thickness of about 500 Å by nitriding vacuum-evaporated Mn films with NH<sub>3</sub> gas at 300°C [9]. The nitride film has a f.c.t. structure with the lattice constants a=4.214 Å, c=4.144 Å. The specimen composition is Mn<sub>8</sub>N<sub>5.32</sub>. They reported that its crystal structure is of the NaCl type with a random distribution of N atoms among the octahedral interstices. Moreover, they found that its tetragonal structure turned to a cubic one at  $683\pm20$  K. They suggested that the phase transition may be related to the magnetic transition, because other compounds in the Mn–N system such as Mn<sub>2</sub>N [5] and Mn<sub>4</sub>N [10] are known to be magnetic materials.

The NaCl and ZnS structures are considered so far as possible crystal structures for the AB type compound of 3d transition metal nitrides. The AB type nitrides of scandium, titanium, vanadium and chromium have the NaCl type f.c.c. structure at room temperature [11–13,16]. We have recently reported that the FeN, CoN and CrN compounds can be prepared as a single phase by DC reactive sputtering [14–16]. The FeN and CoN compounds have not the NaCl type structure but the ZnS type f.c.c. structure [14,15]. We have also investigated the magnetic properties of FeN [14] and CoN [15].

The physical properties of the  $\theta$  phase in the Mn–N system have been little studied, probably because of the difficulty of specimen preparation. In this paper, it is reported that the manganese nitride MnN was prepared by the same method described in Refs. [14,15] and [16]. Then the crystal structure and the thermal stability of the

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prepared MnN compound were examined. The magnetic properties were also investigated.

#### 2. Experimental procedure

The Mn–N sample was prepared by a high rate-type triode DC reactive sputtering [14–16] in a mixture gas of Ar+N<sub>2</sub>. The sputtering conditions were as follows: target voltage, 0.22 kV; target current, 50 mA; total gas pressure,  $3.0 \times 10^{-2}$  Torr; N<sub>2</sub> partial gas pressure,  $0.80 \times 10^{-2}$  Torr; residual gas pressure,  $2.0 \times 10^{-7}$  Torr; and target–substrate distance, 23 mm. A manganese disk of 99.9 percent purity was used as a target, and a water-cooled Cu plate was used as a substrate. The thickness of the deposited Mn–N film was about 130 µm and it was stripped off from the substrate mechanically. This stripped film was powdered. Finally, the powder sample was stress relieved by annealing in vacuum at 510 K for 4 h.

The nitrogen content in the prepared sample was analyzed by gas chromatography, and the manganese content was analyzed by ICP emission spectroscopy. The crystal structure was examined by powder X-ray diffraction using CuK $\alpha$  radiation. In order to prevent preferred orientation of the sample, a mixture of powdered Mn–N compound and quartz powder was used as the sample for the X-ray diffraction. The mixing ratios of the sample powder to quartz powder are from 1 to 0.6.

In order to examine the thermal stability of the Mn–N compound, powder samples were annealed at successively higher temperatures for 2 h. After each annealing, the crystal structure was examined at room temperature. The magnetic properties of the powder sample were measured with a VSM magnetometer

#### 3. Results and discussion

#### 3.1. Chemical and X-ray diffraction analyses

According to the result of gas chromatography, the nitrogen content was 46.6 at.% N, and according to that of ICP emission spectroscopy, the manganese content 48.7 at.% Mn. From the result of gas chromatography, the residue was found to be oxygen. Consequently the N content of the prepared Mn–N compound is estimated to be more than 48 at.% N. Therefore, the atomic ratio of manganese to nitrogen is almost 1:1.

Fig. 1 shows the X-ray diffraction pattern for the stress relieved powdered Mn–N compound. All the diffraction lines were well indexed as the f.c.t. structure. The lattice constants of the f.c.t. structure are a=4.256 Å and c=4.189 Å with c/a 0.9843. The values of lattice constants



Fig. 1. Diffraction pattern for the powdered MnN compound.

are a little larger than those obtained by Lihl et al. [1] and Otsuka et al. [9]. The value of c/a is almost the same as obtained by Lihl et al. and Otsuka et al.

In the case of the f.c.t. structure as well as the f.c.c. one, it is considered that the AB compound has either the NaCl type structure or the ZnS type one. The atom positions in the NaCl type structure and the ZnS type one are written respectively in summary form as:

4 Mn at  $(0\ 0\ 0)$  + face centering translations. 4 N at (1/2, 1/2, 1/2) + face centering translations.

and

4 Mn at  $(0\ 0\ 0)$  + face centering translations. 4 N at (1/4, 1/4, 1/4) + face centering translations.

The difference in the atom positions between the two structures is reflected on the structure factors, and causes a large difference in the ratio of the diffraction line intensities.

In Fig. 2, the experimental diffraction line intensities were compared with the values calculated for the MnN f.c.t. structure of the NaCl type and the ZnS type. The calculated and experimental intensities are normalized to the (111) line intensity. Here, the Debye temperature of 530 K is used in the temperature factor for the calculations. In the calculations of the structure factors, we used atomic scattering factors of neutral atoms [17].

For the NaCl type structure

$$|F|^2 = 16(f_{Mn} + f_N)^2$$
 when  $(h + k + l)$  is even  
 $|F|^2 = 16(f_{Mn} - f_N)^2$  when  $(h + k + i)$  is odd

For the ZnS type structure

 $|F|^{2} = 16(f_{Mn}^{2} + f_{N}^{2}) \text{ when } (h + k + l) \text{ is odd}$   $|F|^{2} = 16(f_{Mn} - f_{N})^{2} \text{ when } (h + k + l) \text{ is an odd multiple}$ of 2  $|F|^{2} = 16(f_{Mn} + f_{N})^{2} \text{ when } (h + k + l) \text{ is an even multiple}$ of 2

where  $(h \ k \ l)$  are the indices of the diffraction lines, and  $f_{\rm Mn}$  and  $f_{\rm N}$  are the atomic scattering factors of the Mn and N atoms, respectively.

The above formulas indicate that the difference in intensities between two structures becomes distinct when the values of (h+k+l) are 2 and 6. As can be seen in the figure, the calculated values for the NaCl type structure agree well with the experimental values. However, those of the ZnS type structure are substantially smaller than the experimental values, especially at the (200) (002), (222) and (420) (402) (204) lines. The values of the reliability factor for the NaCl type structure and the ZnS type one are 11.2% and 42.3% respectively. From these results, the crystal structure of the MnN compound is considered to be the f.c.t. structure with the NaCl type (Fig. 3). This result







Fig. 3. Crystal structure of the MnN compound.

is consistent with that reported by Otsuka et al. The MnN compound prepared in this experiment belongs to the  $\theta$  phase.

#### 3.2. Thermal stability

In order to investigate the thermal stability and the decomposition process of MnN, X-ray diffraction measurements were carried out at room temperature for the samples annealed in vacuum for 2 h at successively higher temperatures between 673 K and 1183 K. The results show that

- 1. The MnN phase is stable up to 753 K.
- 2. At 758 K an extra line appears in addition to those for the f.c.t. MnN compound. This line is well indexed as a super lattice line on the basis of the crystal structure of  $\eta$ -Mn<sub>3</sub>N<sub>2</sub> with ordered vacancies on the N sites of MnN. The unit cell of the  $\eta$ -Mn<sub>3</sub>N<sub>2</sub> compound is formed by removing N atoms from three unit cells of the f.c.t. MnN compound stacked along the direction of the c-axis. The c-planes of the f.c.t. MnN compound have no N atoms every three layers. The lattice constants of a sample annealed at about 800 K are obtained to be a' = 4.205 Å, c' = 12.126 Å at room temperature. These values are in good agreement with the values obtained for  $\eta$ -Mn<sub>3</sub>N<sub>2</sub> by Kreiner et a1. [7]. Only the  $\eta$ -phase exists as a single phase between 758 K and 843 K.
- 3. A part of the  $\eta$ -phase begins to decompose and the

 $\zeta\text{-phase}$  appears at 848 K. The  $\eta\text{-phase}$  and  $\zeta\text{-phase}$  coexist between 848 K and 893 K.

- The η-phase decomposes wholly to the ζ-phase at 898 K. Only the ζ-phase exists as a single phase between 898 K and 978 K.
- 5. A part of the  $\zeta$ -phase begins to decompose and Mn<sub>4</sub>N appears at 983 K. The Mn<sub>4</sub>N compound and the  $\zeta$ -phase coexist between 983 K and 1063 K.
- 6. Only  $Mn_4N$  exists above 1068 K.

The results are summarized in Table 1

In Fig. 4 the lattice constants of the MnN and  $\eta$ -Mn<sub>3</sub>N<sub>2</sub> compound are plotted against the annealing temperatures  $(T_{an})$  in the range from 643 K to 843 K. Here, the lattice constants *a* are derived from the (200) lines, *c* from the (002) lines in the X-ray diffraction patterns. In the figure, the lattice constant *a* and *c* of MnN are shown with the open and closed circles and *a'* and (1/3)c' of Mn<sub>3</sub>N<sub>2</sub> with the open and closed triangles.

As seen in the figure, the *a* and *c* of the MnN compound decrease gradually between about 670 K and 750 K. This is attributed to a statistical absence of N atoms from the compound. As shown in the figure, the MnN compound decomposed abruptly to the  $\eta$ -Mn<sub>3</sub>N<sub>2</sub> compound between 753 K and 758 K. In the process of decomposing, the values of the lattice constant *c* decrease remarkably in comparison with those of *a*. This indicates that a rapid loss of N atoms in the *c*-plane occurs around 755 K.

In order to examine the real ratio of nitrogen to manganese, chemical analysis was carried out for the samples annealed at 738 K and 800 K. According to the results of the analysis for the sample annealed at 738 K, the nitrogen content was 39.7 at.% N, the manganese content 52.7 at.% Mn. The residue was found to be

Table 1

Results of the X-ray diffraction measurements for the MnN compound annealed in vacuum for 2 h at various temperatures

Annealing temperature	Phase analysis
(K)	
673	θ (MnN)
713	θ (MnN)
738	θ (MnN)
753	θ (MnN)
758	$\eta (Mn_3N_2)$
800	$\eta (Mn_3N_2)$
843	$\eta (Mn_3N_2)$
848	$\eta (Mn_3N_2) + \zeta$
893	$\eta (Mn_3N_2) + \zeta$
898	ζ
933	ζ
978	ζ
983	$\zeta + \varepsilon (Mn_4N)$
1033	$\epsilon (Mn_4N) + \zeta$
1063	$\epsilon (Mn_4N) + \zeta$
1068	$\epsilon (Mn_4N)$
1133	$\varepsilon$ (Mn <sub>4</sub> N)
1183	$\varepsilon$ (Mn <sub>4</sub> N)



Fig. 4. The lattice constants of the MnN and  $\eta$ -Mn<sub>3</sub>N<sub>2</sub> compound plotted against the annealing temperatures (T<sub>an</sub>). where  $\bigcirc$  is *a*,  $\bullet$  is *c* of the MnN and  $\triangle$  is *a'*,  $\blacktriangle$  is (1/3)*c'* of the  $\eta$ -Mn<sub>3</sub>N<sub>2</sub>.

oxygen. The nitrogen content of MnN at 738 K is estimated to be 37.7 at.% N. The same analysis was performed for the sample annealed at 800 K. The nitrogen content was 34.0 at.% N and the manganese content 57.1 at.% Mn. The residue was found to be oxygen. The nitrogen content of  $\eta$ -Mn<sub>3</sub>N<sub>2</sub> at 800 K is estimated to be 29.8 at.% N. It is known that the  $\eta$ -phase has some nitrogen concentration range (38.2~41.0 at.% N) [1]. The present result shows that the  $\eta$ -phase has a broader range than that found by Lihl et al. [1].

### 3.3. Magnetic properties

Fig. 5 shows the temperature dependence of magnetization at 10 kOe in the temperature range from 300 K to 800 K. The magnetization increases gradually with increasing temperature in the range from 300 K up to about 640 K and has a broad maximum around 650 K. With further increase of temperature the magnetization decreases, but its temperature dependence does not follow the Curie–Weiss law.

Fig. 6 shows the magnetization curves at room temperature. The magnetization increases linearly with the field. The susceptibility  $x_g$  is obtained to be  $2.15 \times 10^{-5}$  emu g<sup>-1</sup>.

The result suggests that the compound MnN is antiferromagnetic with a Néel temperature around 650 K and the tetragonal distortion is ascribed to an exchange striction by onset of magnetic order. In order to make clear the magnetic properties and the origin of the tetragonal lattice distortion, neutron diffraction and measurements of the temperature variation of lattice constants and heat capacity are now in progress.

## 4. Conclusion

The compound MnN was prepared as a single phase by the DC reactive sputtering method. From the powder X-ray diffraction experiments its crystal structure is determined to be of the face-centered tetragonal one of the NaCl type.



Fig. 5. Temperature dependences of the magnetization for the MnN compound at 10 kOe.



Fig. 6. Magnetization curves for the MnN compound at room temperature.  $\bullet$ : increasing magnetic field.  $\bigcirc$ : decreasing magnetic field.

The lattice constants are obtained to be a=4.256 Å and c=4.189 Å. The MnN compound is stable up to 753 K, and decomposes into the Mn<sub>3</sub>N<sub>2</sub> compound with tetragonal structure at 758 K. From the magnetic measurements the compound MnN was found to be antiferromagnetic.

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